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IN SEARCH OF AN IDEALIZED MODEL OF
HOMOGENEOUS SOLID PROPELLANT
COMBUSTION

Martin S. Miller

December 1981



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
BALLISTIC RESEARCH LABORATORY
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20. ABSTRACT (Continued)

are shown to lead explicitly to approximate analytic expressions of the same functional form as empirical formulas for the burning rate pressure dependence. The approximation developed in this paper is shown to lead to a common empirical form for the temperature sensitivity. A means of testing the suitability of these approximations to a given propellant is also developed using temperature profiles obtained by the embedded thermocouple technique.

TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS	5
I. INTRODUCTION	7
II. FORMULATION OF THE 1-DIMENSIONAL STEADY-STATE PROBLEM	7
A. General Approach	7
B. Gas Phase Description	8
C. Solid Phase Description	13
D. Surface Decomposition Mechanism	14
E. Solution Matching at the Interface	16
F. Simplifications	17
III. GAS-PHASE APPROXIMATIONS	18
A. Constant Temperature Reaction Rate (CTRR)	18
B. Delta Function Heat Release (DFHR)	20
C. Quasi-Constant Heat Release (QCHR)	23
D. Review of Experimental Evidence for Gas Phase	25
IV. ANALYTIC BURNING RATE EXPRESSIONS	31
A. Pyrolysis Decomposition Mechanism	32
1. CTRR Approximation to ϕ_G	34
2. DFHR Approximation to ϕ_G	37
3. QCHR Approximation to ϕ_G	39
B. Evaporation Decomposition Mechanism	40
1. CTRR Approximation to ϕ_G	40
2. DFHR Approximation to ϕ_G	41
3. QCHR Approximation to ϕ_G	41
C. Discussion	41
V. SUMMARIZING REMARKS	43
ACKNOWLEDGEMENT	45
REFERENCES	46
LIST OF SYMBOLS	49
DISTRIBUTION LIST	53

LIST OF ILLUSTRATIONS

Figures	Page
1. Schematic Representation of Processes Considered in Burning of Idealized Solid Propellant	9
2. Empirical Gas-Phase Heat Release Function Calculated by Klein, et al., ¹⁸ for NC at 28 atm	27
3. Empirical Gas-Phase Heat Release Function Based on Data of Kubota, et al., ¹⁷ for PNC/TMETN at 1.2 atm.	28
4. Empirical Gas-Phase Heat Release Function Based on Data of Kubota, et al., ¹⁷ for PNC/TMETN at 21 atm.	29
5. Illustration of Matching Condensed and Gaseous Phase Heat Fluxes in Order to Obtain Surface Temperatures for a Given (T_o , P) in the Case of a Pyrolysis Mechanism.	33

I. INTRODUCTION

The present paper is concerned with the theoretical description of steady-state deflagration of uncatalyzed, homogeneous solid propellants. Our principal aim is to seek a minimum level description of the burning process which can elucidate the relationship between the fundamental chemical and physical properties of a propellant and such combustion characteristics as the pressure and temperature sensitivities. It is our feeling that such a description must involve processes occurring in both the condensed and gaseous phases and account for their mutual interplay at the phase boundary. Accordingly, the basic idealization of the burning process to be considered in this paper is that of a single gas-phase chemical reaction and a single condensed-phase process responsible for surface gasification. Both sublimation (or evaporation from a melt layer) and pyrolysis into gaseous products are considered as candidate possibilities for this gasification process.

The chosen idealization is by no means novel; however, the considerable literature on the subject is marked by diversity in notation, approach, and intent. Comparison of burning rate predictions is hampered by these characteristics and, more importantly, by the fact that many theories are not strictly expressible in closed form. In this paper we derive approximate closed form expressions for the burning rate pressure and temperature dependences based on what we perceive to be the salient assumptions of a number of these theories. Within the mathematical framework adopted for this study most theories fall into one of three broad categories of heat feedback approximation. Naturally, some theories fit into our scheme better than others, hence no judgement is implied regarding those theories lightly touched on or not mentioned at all.

Progress toward the understanding of complex phenomena has often been made through the use of idealizations. It is unfortunate that the subject idealization, primitive as it may seem, appears not to be amenable to exact solution. Expressing the gas-phase reaction rate in an Arrhenius form (as is usual) introduces extreme non-linearities into the conservation equations, making even numerical solutions far from trivial. Notwithstanding this fact and the enormous potential detail which might be required to characterize the gas-phase processes for each propellant, the observed burning rate as a function of both pressure and initial temperature displays a remarkably simple and universal behavior. This suggests that insight might be gained regarding at least the broad features of the combustion phenomenology through development of an appropriate idealization. The present study represents an attempt to determine the adequacy of existing notions for this purpose.

II. FORMULATION OF THE 1-DIMENSIONAL STEADY-STATE PROBLEM

A. General Approach

At our chosen level of idealization, the solid propellant burning process consists of one mole of unburnt propellant molecules A in the solid undergoing a physical or chemical transformation into N_1 moles of gaseous B molecules. Each mole of B molecules then reacts chemically in the gas phase to produce N_2 moles of product molecules C. The gas-phase reactant B may be either the same

chemical species as A (differing only by a phase change) or a different chemical species than A. Figure 1 represents these processes schematically. In principle, the problem can be approached by solving the steady-state conservation equations in the solid and gas phases separately and then matching the solutions at the gas-solid interface in a manner consistent with the assumed solid-to-gas decomposition mechanism.

B. Gas Phase Description

The gas-phase problem consists of only two different chemical species, denoted by B and C. It is supposed that B undergoes reactive conversion to C with the consequent release of heat. Our problem is to compute the conductive heat feedback to the surface of the solid under constant pressure conditions. The radiative component of the heat feedback is assumed to be negligible. As mentioned, if one expresses the reaction rate in an Arrhenius form, the conservation equations take on a highly non-linear character, placing an exact solution beyond reach. For this reason some investigators have obtained approximate solutions in an attempt to gain an appreciation for the interrelation of physical and chemical processes. However, even these approximate solutions are sometimes so mathematically involved as to endanger their purpose. Such analytic intricacy inhibits comparison of the salient features of these theories as well. It is our intent to re-examine this approach by expressing the essential elements of a number of these past approximations in a single framework which hopefully clarifies their physical implications.

The conservation equations for the steady-state include those for mass, chemical species, and energy given respectively as¹

$$\frac{d}{dx} (\rho u) = 0 \quad \text{Mass Conservation}$$

$$\frac{d}{dx} (m_B \rho V_B) + R(x) = 0 \quad \text{Chemical Species Conservation}$$

$$\frac{d}{dx} \left(\lambda \frac{dT}{dx} \right) - \frac{d}{dx} (m_B \rho h_B V_B + m_C \rho h_C V_C) = 0 \quad \text{Energy Conservation}$$

where ρ is the local mass density of the gas mixture, u is the local velocity of mass motion, m_B and m_C are the local mass fractions of species B and C, V_B and V_C are the local species velocities (combined mass motion and diffusional components), $R(x)$ is the mass of B undergoing reaction per unit volume per unit time at x , λ is the local thermal conductivity of the mixture, T is the local temperature, and $h_{B,C}$ is the local enthalpy per unit mass for species B or C. A chemical species equation can be written analogously for m_C . The mass con-

¹R.D. Geckler, "The Mechanism of Combustion of Solid Propellants," *Selected Combustion Problems*, AGARD, Butterworths (London), 1954. p. 289.

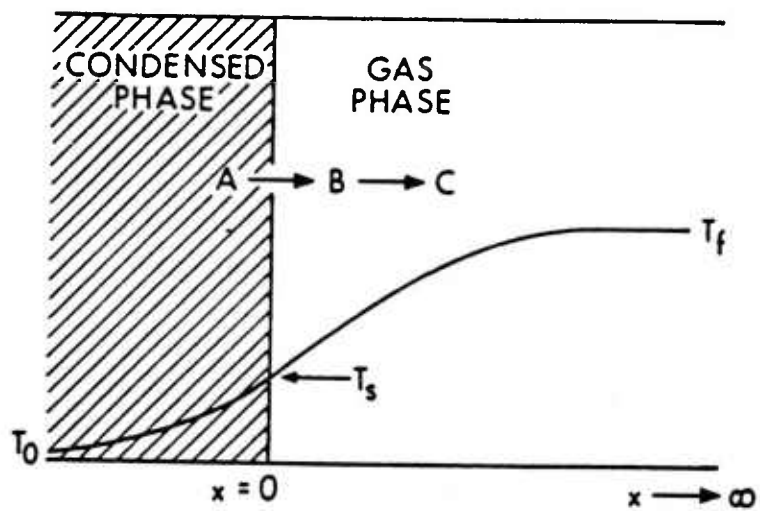


Figure 1. Schematic representation of processes considered in burning of idealized solid propellant.

servation equation can be integrated to obtain

$$\rho u = \text{constant} \equiv M \quad (1)$$

where M is sometimes called the mass regression rate and is related to the linear regression rate r through the solid density ρ_s by the equation

$$M = \rho_s r \quad (1a)$$

If we assume negligible particle diffusion by thermal gradient (Soret effect), the species mass fluxes can be written

$$m_B \rho V_B = m_B \rho u - D \rho \frac{dm_B}{dx} \quad (2)$$

and analogously for m_C , where D is the diffusion coefficient ($D_B = D_C = D$)².

The species conservation equation can then be written

$$\frac{d}{dx} (D \rho \frac{dm_B}{dx}) - M \frac{dm_B}{dx} - R(x) = 0 \quad (3)$$

and the energy conservation equation becomes

$$\frac{d}{dx} (\lambda \frac{dT}{dx}) - M C_p \frac{dT}{dx} + (h_B - h_C) R = \rho D \frac{dm_B}{dx} \frac{dT}{dx} (C_p^C - C_p^B)$$

where the specific heat of the mixture, C_p , is related to the component specific heats C_p^B and C_p^C by $C_p = m_B C_p^B + m_C C_p^C$. We now make the first substantive assumptions,

$$C_p^B = C_p^C = C_p = \text{constant}$$

$$\lambda = \text{constant}$$

With the first of these assumptions, the energy equation becomes

$$\frac{d}{dx} (\lambda \frac{dT}{dx}) - M C_p \frac{dT}{dx} + q(x) = 0 \quad (4)$$

where

$$q(x) = (h_B^{\circ} - h_C^{\circ}) R(x) = Q_G R(x) \quad (5)$$

the symbol $Q_G \equiv h_B^{\circ} - h_C^{\circ}$ being used to represent the heat of reaction per unit reactant mass in the gas phase at the reference thermodynamic state (denoted by the zero superscripts). Making use of the $\lambda = \text{constant}$ assumption and imposing the boundary condition

$$\left. \frac{dT}{dx} \right|_{x=\infty} = 0$$

Eqn. (4) may be integrated by the integrating factor method to give the conductive heat feedback flux ϕ_G

$$\phi_G \equiv \lambda \left. \frac{dT}{dx} \right|_{x=0} = \int_0^{\infty} \exp\left(-\frac{MC_p}{\lambda} x\right) q(x) dx. \quad (6)$$

As it stands Eqn. (6) is purely a formal result since $q(x)$ is only known after the problem has been solved; however, it is a particularly meaningful equation from a physical standpoint. The exponential factor

$$\exp\left(-\frac{MC_p}{\lambda} x\right)$$

is a measure of the relative effectiveness with which heat released at some distance x from the surface contributes to the overall heat feedback. As might be expected, the larger λ is, the more effective is the heat conduction back to the surface. The larger C_p is, the more heat is retained at x and the less heat is returned to the surface. The larger M is, the more difficult it is for heat to return to the surface against the convective counter-flow.

The gas-phase heat release function $q(x)$ can be related to the physical and kinetic parameters of the gas phase as follows:

$$q(x) = Q_G R(x) = Q_G (m_B \rho)^{\nu} k_G \quad (7)$$

where ν is the reaction order and k_G is the reaction rate constant assumed to have the form (R being the universal gas constant)

$$k_G = A_G e^{-E_G/RT} \quad (8)$$

Expressing ρ in terms of the ideal gas law,

$$\rho = \frac{\bar{W}P}{RT} \quad (9)$$

where \bar{W} is the mean molecular weight of the gas mixture. As previously noted, N_2 moles of C appear for every mole of B that reacts so that the molecular weight of C, W_C , is related to the molecular weight of B, W_B , by $W_C = W_B/N_2$. The number of moles of B and C at any x , n_B and n_C , is given by

$$n_B = \frac{m_B \rho}{W_B} \quad n_C = \frac{m_C \rho}{W_C} = \frac{(1-m_B) \rho N_2}{W_B}.$$

The average molecular weight at this point in the gas can therefore be shown to be

$$\bar{W} = \frac{W_B}{N_2 - m_B(N_2 - 1)}. \quad (10)$$

Combining Eqns. (7), (8), (9), and (10),

$$q(x) = \frac{Q_G m_B^v W_B^v P^v A_G e^{-E_G/RT}}{R^v T^v [N_2 - m_B(N_2 - 1)]^v} \quad (11)$$

where it is understood that m_B and T are functions of x .

A number of other useful relationships can be obtained by making the further assumption that the Lewis number is unity, in which case

$$D\rho = \frac{\lambda}{C_p} \cdot \quad (12)$$

Physically, this assumption links the heat transfer by conduction to that transported by diffusion. Mathematically, Eqns. (3) and (4) are no longer independent, i.e., the solution of one can be related to the solution of the other. Using Eqn. (12) one can show² that the enthalpy is uniform throughout the gas phase, i.e., if we follow a unit mass sample from the surface at temperature T_s to the final flame temperature T_f , the enthalpy of the sample

²D.B. Spalding, "The Theory of Burning of Solid and Liquid Propellants," *Combustion & Flame*, Vol. 4, p. 59 (1960).

at any point is given by

$$m_B(T) h_B(T) + m_C(T) h_C(T) = h_C(T_f) \quad (13)$$

where h_B is the enthalpy of B per unit mass of B, etc. By our previous assumption that $C_p^B = C_p^C = C_p = \text{constant}$, we can write, for example,

$$h_B = h_B^\circ + C_p (T - T^\circ) \quad (14)$$

Substituting Eqn. (14) and the analogous expression for h_C into Eqn. (13) and making use of the constraint $m_B + m_C = 1$, one can show that

$$m_B(T) = \frac{C_p (T_f - T)}{Q_G} \quad (15)$$

which relates the solution of Eqn. (3) to that of Eqn. (4) at all x in the gas phase.

C. Solid Phase Description

In this section the external energy flux required by the solid in order to maintain a given steady-state M and T_s will be determined. We shall neglect any radiative energy loss from the solid. (See Section IVC for further comment on this assumption). It is envisioned that the solid-to-gas decomposition comprises the following sequence of steps. At $x = -\infty$ the solid is entirely A so that $m_A = 1$. In the case of a pyrolysis reaction it is assumed that a unit mass of A will be converted into m_B^{-0} unit mass of B and $(1 - m_B^{-0})$ unit mass of C. Thus at $x = -0$, i.e., at the condensed-phase side of the interface, $m_A = 0$, $m_B = m_B^{-0}$, and $m_C = (1 - m_B^{-0})$. At this stage B and C are considered to be adsorbed onto the surface. Since the symbols h_B and h_C refer to the gaseous phase of B and C, we shall denote the enthalpy of B and C in the absorbed state by $h_{B,s}$ and $h_{C,s}$. Taking $m_B^{-0} \neq 1$ in general allows us to consider the case where both reactive as well as non-reactive products are formed in the condensed-phase pyrolysis reaction. For simplicity we have assumed that these non-reactive products have the same properties as C. B is assumed to react only in the gas phase.

The steady-state energy conservation equation in the condensed phase, neglecting particle diffusion, may be written

$$\frac{d}{dx} \left(\lambda_s \frac{dT}{dx} \right) - M C_s \frac{dT}{dx} + q_s(x) = 0 \quad (16)$$

where λ_s is the thermal conductivity of the solid, C_s its specific heat, and $q_s(x)$ the heat absorbed by the solid per unit volume per unit time from reactions in the solid. C_s is assumed to be constant. Integrating Eqn. (16)

from $x = -\infty$ to $x = -0$ with the boundary condition $\frac{dT}{dx}|_{x=-\infty} = 0$, we obtain

$$\phi_S' \equiv \lambda_s \frac{dT}{dx}|_{x=-0} = MC_s(T_s - T_o) - M [h_A^o - m_B^{-o} h_{B,s}^o - (1 - m_B^{-o}) h_{C,s}^o] \quad (17)$$

The last term in Eqn. (17) may be obtained by constructing $q_s(x)$ by analogy to Eqn. (5) and integrating the species conservation equation of m_A (similar to Eqn. (3) but with zero diffusion) from $x = -\infty$ to $x = -0$.

As noted by Buckmaster, et al.,³ there is an additional energy flux requirement arising from the desorption of B and C at the interface. In our notation it is given by

$$\phi_I = M m_B^{-o} [h_B(T_s) - h_{B,s}(T_s)] + M (1 - m_B^{-o}) [h_C(T_s) - h_{C,s}(T_s)]$$

Since $h_{B,s}(T) = h_{B,s}^o + C_s(T - T^o)$ and $h_B(T) = h_B^o + C_p(T - T^o)$, etc., the total energy flux requirement can be shown to be

$$\phi_S = \phi_S' + \phi_I = MC_p(T_s - \frac{C_s}{C_p} T_o - \frac{Q_s}{C_p}) \quad (18)$$

where $Q_s \equiv h_A^o - m_B^{-o} h_B^o - (1 - m_B^{-o}) h_C^o + (C_s - C_p) T^o$. ϕ_S in Eqn. (18) simply represents the heat flux required from sources external to the solid to maintain a surface temperature T_s when the mass regression rate is M and the initial temperature is T_o . ϕ_G , on the other hand, is the heat flux which the gas-phase processes are capable of providing at a given pressure when the mass flux is M and the surface temperature is T_s .

We shall also wish to examine a simple phase change process as the mechanism for surface gasification. In this case $m_B^{-o} = 1$ and Eqn. (18) is changed only by the substitution $Q_s = -Q_v$, where Q_v is the latent heat of transformation.

D. Surface Decomposition Mechanism

In addition to having to solve the conservation equations for the gas and solid phases separately, one must also have a quantitative description of the mechanism by which the solid decomposes into a gas at the interface. The details of this process are poorly understood despite its central importance to propellant combustion. There are, however, two schools of thought which have found recurring application. One is that the mechanism consists of pyrolytic conversion of solid reactant to gas-phase products. The other is that the

³J.D. Buckmaster, A.K. Kapila and G.S.S. Ludford, "Linear Condensate Deflagration for Large Activation Energy," *Acta Astronautica*, Vol. 3, p. 593 (1976).

conversion is a phase change between condensed and gaseous states, i.e., either sublimation or evaporation from a melt layer.

The pyrolysis hypothesis is usually expressed by the relation

$$M = M_0 e^{-E_s/RT_s} . \quad (19)$$

There have been few attempts to estimate M_0 and E_s in an *a priori* sense.^{4,5} The calculation of Wilfong, Penner and Daniels⁴ was based on the energy needed to break the O-NO₂ bond in nitrocellulose (NC), the surface density of those bonds, and application of transition state theory to obtain a frequency factor. The value of this frequency factor, although typical for gas-phase unimolecular reactions, is five or more orders of magnitude lower than that derived from NC thermal decomposition experiments.^{1,6,7} In most cases, however, M_0 and E_s are simply used as fitting parameters to calibrate a given burning rate model to experimental data.

Evaporative mechanisms usually take the integrated Clausius-Clapyron form for the propellant vapor pressure (P_B) immediately adjacent to the surface, i.e.,

$$P_B = P_0 e^{-E_v/RT_s} \quad (20)$$

where E_v is the heat of vaporization and P_0 is a constant. Use of this equilibrium-based expression may have validity as an idealization in spite of the inherently non-equilibrium phenomenon of burning. One can expect that equilibrium would be established at a rate which depends on the molecular velocity (of molecules escaping the surface). The vapors outside the surface are removed at a rate depending on the transport velocity (V_B in Eqn. (2)). The molecular

⁴R.E. Wilfong, S.S. Penner and F. Daniels, "An Hypothesis for Propellant Burning," *J. Phys. & Colloid Chem.*, Vol. 54, p. 863 (1950).

⁵R.D. Schultz and A.O. Dekker, "The Absolute Thermal Decomposition Rates of Solids," *Fifth Symposium (International) on Combustion, The Combustion Institute* (1960), p. 260.

⁶R.D. Smith, "Pyrolysis of Dissolved Nitrocellulose," *Nature*, Vol. 170, p. 844 (1952).

⁷R.W. Phillips, C.A. Orlick and R. Steinberger, "The Kinetics of the Thermal Decomposition of Nitrocellulose," *J. Phys. Chem.*, Vol. 59, p. 1034 (1959).

velocity, however, should be fast relative to the transport velocity or the notion of local temperature would break down. It is reasonable, therefore, to assume that at least a condition of "near" equilibrium vapor pressure might well prevail very close to the surface.

E. Solution Matching at the Interface

The conservation laws which are applied in obtaining ϕ_G and ϕ_S , viz., conservation of mass, energy and species, must also be applied to the solid-gas interface. In addition, the solid decomposition mechanism must be taken into account. The mass conservation principle is satisfied simply by requiring that M have the same value in both the solid and gas phases. Energy conservation is achieved by equating the energy fluxes across the interface, i.e.,

$$\phi_S(T_S, M) = \phi_G(T_S, M). \quad (21)$$

In physical terms, this means that the energy flux required by the solid to maintain a steady-state mass regression rate M at a surface temperature T_S must be supplied by the heat flux which the gas-phase processes are capable of providing for the same values of M and T_S .

Species conservation across the interface is assured by the formulation of an appropriate boundary condition. Since we are assuming that no diffusion occurs in the condensed phase, the flux of B at the left of the boundary is Mm_B^{-0} . This value is reduced on the gas side of the boundary by diffusion. The continuity condition is then

$$Mm_B^{-0} = Mm_B^{+0} - D\rho \left. \frac{dm_B}{dx} \right|_{x=+0} \quad (22)$$

Since m_B is decreasing in the gas phase, the derivative on the right side of Eqn. (22) will be negative, so that $m_B^{-0} > m_B^{+0}$ as expected. Normally, Eqn. (22) would be used as a boundary condition in solving Eqn. (3) in order to obtain $\phi_G(T_S, M)$. This is done in Section IIIA where by assuming a constant temperature reaction rate an analytic solution can be found. It would also be done in a numerical solution to Eqns. (3) and (4). In one of the approximations to be discussed (Section IIIC) we shall find it convenient to view Eqn. (22) simply as a constraint to be observed in matching the heat fluxes (Eqn. (21)). In this connection it is useful to place Eqn. (22) in a slightly different form. Using Eqn. (15) to relate the derivatives of m_B and T , and substituting for $D\rho$ from Eqn. (12), we find

$$m_B^{-0} = m_B^{+0} + \frac{\phi_G}{Q_G M} \quad (23)$$

In addition to these continuity requirements an additional constraint is imposed by the surface decomposition mechanism. For pyrolysis $M(T_S)$ is given by Eqn. (19). The phase change mechanism quantified by Eqn. (20) does not

explicitly relate the unknowns T_s, M , and m_B^{+0} , so that the nature of the constraint is not clear. Starting from the relation $P = P_B + P_C$, where P_C is the partial pressure of C, and using Eqn. (10), one can arrive at the expression

$$m_B^{+0}(T_s) = \frac{N_2 P_B(T_s)}{P + (N_2 - 1) P_B(T_s)} \quad (24)$$

Eqn. (24), where $P_B(T_s)$ is given by Eqn. (20), is then the most convenient operational constraint corresponding to the phase change mechanism.

In summary, one can view the problem of finding the steady-state solution as one in which the three unknowns, T_s, M, m_B^{+0} are to be found from Eqns. (21), (23), and either Eqn. (19) or Eqn. (24). The way in which this is done will depend in detail on the approximation method used, a matter which will be discussed in Section III.

F. Simplifications

For purposes of making first order comparisons of different theories for $\dot{\phi}_G$, much of the detail of previous sections is not needed. In particular, we wish to simplify the problem by holding constant those variables whose expected degree of change would be unlikely to seriously influence results. The following items are so identified and appropriately approximated as

$$\bar{W} = \text{constant}$$

$$C_s = C_p \equiv \bar{C}_p \quad (25)$$

It is assumed that in applying these approximations one has sufficient information on a propellant to make reasonable estimates for these constants.

A further simplification we shall wish to make is to assume negligible species transport by diffusion. The quality of this approximation is by no means self-evident, and can best be assessed by comparison to a calculation which does not neglect diffusion. Rice and Ginell⁸ have done this and found that the character of the burning rate behavior is not seriously altered by this assumption. It is important to note that in the zero diffusion limit we can no longer assume that the Lewis number is unity as this would force a neglect of thermal conduction (by Eqn. (12)) as well. With no diffusion the species transport equation (Eqn. (3)) can then be written

$$M \frac{dm_B}{dx} = - R(x) \quad (26)$$

⁸O.K. Rice and R. Ginell, "The Theory of the Burning of Double-Base Rocket Powders," *J. Phys. & Colloid Chem.*, Vol. 54, p. 885 (1950).

and the boundary condition of Eqn. (22) becomes

$$m_B^{+0} = m_B^{-0} \quad (27)$$

For both pyrolysis and evaporation mechanisms this assumption has the effect of reducing the unknowns to only T_s and M , eliminating Eqn. (23).

For convenience we label the approximations expressed in Eqns. (25)-(27) as Level II. A Level I calculation is taken to imply all of the assumptions stated in the development prior to Eqn. (25). Thus a Level I calculation is our most general formulation of the basic idealization. A Level II calculation is an approximate formulation from which general trends are still expected to emerge. In this paper we shall devote the bulk of our attention to the Level II approximation since here our primary interest is in qualitative trends implied by the chosen idealization. The problem of applying these concepts to actual propellant formulations in a Level I calculation requires the difficult choice of kinetic constants and will be addressed in a future article.

III. GAS-PHASE APPROXIMATIONS

In this section we shall consider a number of different approaches to estimating the gas-phase heat feedback capability ϕ_G . The utility of the form of Eq. (6) will become clear since all of the approximations discussed can be reduced to assumptions as to the behavior of $q(x)$.

A. Constant Temperature Reaction Rate (CTRR)

It is clear from Eqn. (6) that if an adequate approximation for the heat release function $q(x)$ can be found, ϕ_G can be calculated for a given value of M . Eqn. (11) shows that in order to compute $q(x)$, both $T(x)$ and $m_B(x)$ must be known. These two quantities are interrelated by the energy conservation equation (Eqn. (4)) and the species continuity equation (Eqn. (3)). If we assume that the reaction proceeds as though it were at some constant temperature T_1 (historically taken as the flame temperature, T_f) and with constant \bar{W} , i.e.,

$$R(x) = R_o m_B^v \quad (28)$$

where

$$R_o \equiv \frac{\bar{W}^v P^v A_G e^{-E_G/RT_1}}{R^v T_1^v} \quad (29)$$

then Eqn. (3) can be solved exactly for $v=1$ (using Eqn. (22) as interface

boundary condition). The solution is

$$m_B = \frac{m_B^{-0} e^{-\alpha x}}{(1 + \frac{D\rho}{M} \alpha)} \quad (\text{for } v=1) \quad (30)$$

where

$$\alpha \equiv \frac{M}{2D\rho} \left[\left(\frac{4R_0 D\rho}{M^2} + 1 \right)^{1/2} - 1 \right]$$

Using Eqns. (28) and (30) we may then arrive at an expression for the gas-phase heat feedback ϕ_G by integrating Eqn. (6).

$$\phi_G = \frac{\lambda Q_G R_0 m_B^{-0}}{MC_p (1 + \frac{D\rho\alpha}{M}) (1 + \frac{\lambda\alpha}{MC_p})} \quad (\text{for } v=1) \quad (31)$$

It is of interest to compare this solution which includes the effects of species diffusion to one in which such effects are neglected. This can be accomplished by solving Eqn. (3) without the second derivative term (or taking the limit of Eqn. (30) as $D\rho \rightarrow 0$). Again for $v=1$, the results are

$$m_B = m_B^{-0} e^{-\frac{R_0}{M} x} \quad (v=1, \text{ no diffusion}) \quad (32)$$

and

$$\phi_G = \frac{\lambda Q_G R_0 m_B^{-0}}{MC_p (1 + \frac{\lambda R_0}{M^2 C_p})} \quad (v=1, \text{ no diffusion}). \quad (33)$$

The functional forms of Eqns. (31) and (33) bear some resemblance, and in the limit of small R_0/M^2 the forms become identical. Physically, this limit corresponds to the heat feedback ϕ_G being small compared to the maximum possible heat feedback $Q_G M m_B^{-0}$. (See Section IVA1).

For the case of a second order reaction, i.e., $v=2$, Eqn. (3) appears not to have a closed form solution. However, it can be solved analytically in the

limit of zero diffusion, in which case

$$m_B = \frac{m_B^{-o}}{\left(1 + \frac{m_B^{-o} R_o x}{M}\right)} \quad (v=2, \text{ no diffusion}), \quad (34)$$

The corresponding expression for ϕ_G is

$$\phi_G = Q_G M m_B^{-o} e^{\frac{M^2 C_p}{\lambda R_o m_B^{-o}}} E_2\left(\frac{M^2 C_p}{\lambda R_o m_B^{-o}}\right) \quad (v=2, \text{ no diffusion}) \quad (35)$$

where $E_2(z)$ is the standard exponential integral.

Equation (35) can be related to two of the early attempts to model homogeneous solid propellant combustion. Both Parr and Crawford⁹ and Rice and Ginell⁸ assumed a second order reaction in the "fizz zone" or gaseous region immediately adjacent to the surface of a burning double-base propellant. Parr and Crawford⁹ assumed zero diffusion and arrived at a first approximation (Eqn. (42) of Ref. 9) which is essentially the same expression as a mixture of our Eqns. (18) and (35). Rice and Ginell⁸ at first treated the zero diffusion case and also arrived at an equivalent of our Eqns. (18) and (35) (Cf. Eqns. (9), (10) and (11a) of Ref. 8). These latter authors then introduced a diffusion correction for the second order reaction case and found, as have we for $v=1$ above, that the functional forms of the solution with and without diffusion are similar. Rice and Ginell⁸ justified the use of a constant temperature reaction rate as a limiting case of zero activation energy (E_G) and simply used k_G as an adjustable constant in fitting their theory to burning rate data. Parr and Crawford,⁹ while conceding that zero activation energy is the proper limiting case corresponding to use of Eqn. (29), chose to retain explicitly both the activation energy (E_G) and frequency factor (A_G) as adjustable parameters in fitting their theory to burning rate data. Their rationale was to consider the constant temperature reaction rate as an approximate formulation. In both treatments^{8,9} the temperature T_1 was taken to be that at the end of the fizz zone, i.e., T_f in our notation.

B. Delta Function Heat Release (DFHR)

Another approach to evaluating ϕ_G is to assume that the heat release function $q(x)$ can be approximated by a Dirac delta function, i.e.,

$$q(x) = q_o \delta(x-x^*) \quad (36)$$

⁹R.G. Parr and B.L. Crawford, Jr., "A Physical Theory of Burning of Double-Base Rocket Rocket Propellants," *J. Phys. & Colloid Chem.*, Vol. 54, p. 929, 1950.

where x^* is the so called flame-standoff distance and q_0 can be evaluated by the requirement

$$\int_0^\infty q(x)dx = Q_G^{Mm_B}{}^{-0} \quad (37)$$

which is simply the flux corresponding to the total gas-phase heat release. Eqn. (37) can be obtained by integrating Eqn. (3) over $(+0, \infty)$ subject to the boundary condition Eqn. (22). It follows that the constant in Eqn. (36) is given by

$$q_0 = Q_G^{Mm_B}{}^{-0}. \quad (38)$$

Equation (36) is a reasonable picture of $q(x)$ in the limit of infinitely large activation energy E_G , as can be seen graphically in the laminar flame theory paper of Spalding.¹⁰ The difficulty of using Eqn. (36) is not in its functional form but in evaluating a proper value for x^* . Inserting Eqn. (36) into Eqn. (6) we obtain

$$\phi_G = Q_G^{Mm_B}{}^{-0} e^{-\frac{MC}{\lambda} x^*}. \quad (39)$$

Thus the value of x^* is critical to this approximation.

As representative of the "flame-sheet" models we shall discuss only the model devised by Hermance¹¹ and later incorporated into the BDP composite propellant model.^{12,13} All of these models share the characteristic that the reaction rate is evaluated only at the flame temperature; however, they differ in detail sufficiently that our results will pertain only to the Hermance¹¹/BDP^{12,13} formulation. The other flame-sheet models, of which this writer is

¹⁰D.B. Spalding, "II. One-Dimensional Laminar Flame Theory for Temperature-Explicit Reaction Rates," *Combustion & Flame*, Vol. 1, p. 296 (1957).

¹¹C.E. Hermance, "A Model of Composite Propellant Combustion Including Surface Heterogeneity and Heat Generation," *AIAA Journal*, Vol. 4, p. 1629 (1966).

¹²M.W. Beckstead, R.L. Derr and C.E. Price, "A Model of Composite Solid-Propellant Combustion Based on Multiple Flames," *AIAA Journal*, Vol. 8, p. 220 (1970).

¹³M.W. Beckstead, R.L. Derr and C.E. Price, "The Combustion of Solid Mono-propellants and Composite Propellants," *Thirteenth Symposium (International) on Combustion*, The Combustion Institute (1971), p. 1047.

aware, are due to Culick¹⁴ and Williams.¹⁵ In Culick's model,¹⁴ q_0 is not determined by Eqn. (37) but specified *a priori* as $Q_G R_0$ (defined in Eqn. 29 with $T_1 = T_f$). The argument of the delta function is then expressed in a transformed coordinate. With this specification of q_0 , however, one can show that the derived burning rate formula depends on the coordinate transformation used, thereby invalidating the method. The Williams model¹⁵ avoids the delta function formalism by applying asymptotic analysis to the flame sheet idealization. The resulting solution is functionally similar (though not identical) to the Hermance formulation.

Hermance¹¹ argues for the value of x^* as follows.

$$x^* = U\tau \quad (40)$$

where U is the average velocity of gases flowing away from the solid interface and τ is the average reaction delay time. These quantities are in turn estimated as

$$U = \frac{M}{\rho_f} \quad (41)$$

where ρ_f is the gas density at the flame temperature, and

$$\tau = \frac{1}{\rho_f^{\nu-1} A_G e^{-E_G/RT_f}} \quad (42)$$

Combining (40), (41) and (42) we obtain

$$x^* = \frac{M}{\rho_f^{\nu} A_G e^{-E_G/RT_f}} \quad (43)$$

Hermance considered only $\nu=2$; therefore we have generalized his result to arbitrary reaction order. Use of Eqn. (42) would seem to be inconsistent with the sense in which the delta function might be considered a valid idealization, i.e., in the limit of high E_G . In this limit the reaction is essentially confined to a thin spatial zone whose thickness is small compared with its distance from the surface. The τ required by Eqn. (40) is the mean

¹⁴F.E.C. Culick, "An Elementary Calculation of the Combustion of Solid Propellants," *Astronautica Acta*, Vol. 14, p. 171 (1969).

¹⁵F.A. Williams, "Quasi-Steady Gas-Phase Flame Theory in Unsteady Burning of a Homogeneous Solid Propellant," *AIAA Journal*, Vol. 11, p. 1328 (1973).

time it takes for the gaseous reactants to travel from the surface to the thin reaction zone. The τ represented by Eqn. (42), on the other hand, is related to the time it takes to complete the reaction within the reaction zone. This same expression is used by Rice and Ginell⁸ to describe the zero activation energy limit. It would seem, therefore, that the true value of x^* is underestimated by Eqn. (43), leading to an overestimate of ϕ_G . In the more rigorous treatment of the high E_G limit by Williams¹⁵, however, an expression for x^* can be obtained which is the same as Eqn. (43) except for a multiplicative constant (more precisely, a quantity which is nearly constant). Such a circumstance seems to justify use of Eqn. (43); however, in an actual numerical calculation the multiplicative constant may have a significant effect since x^* appears in an exponent. As we are primarily interested in functional relationships in this paper we may ignore such fine points and treat the Hermance flame standoff as adequately representative of the delta function approach. Substituting Eqn. (43) into Eqn. (39), one obtains

$$\phi_G = Q_G M_B^{-1} \exp \left(- \frac{M^2 C_p R T_f}{\lambda \bar{W} P A_G e^{-E_G/RT_f}} \right) \quad (44)$$

C. Quasi-Constant Heat Release (QCHR)

We have developed an approximation to ϕ_G which is complementary to the CTRR and DFHR limiting cases. The spatial variation of the heat release function is essentially determined by a competition between the decreasing reactant mass fraction m_B and the increasing reaction rate k_G (cf. Eqn. (7)). In the CTRR case the m_B variation dominates so the $q(x)$ is monotonic decreasing. In the DFHR model k_G initially increases faster than m_B decreases so that $q(x)$ increases over most of the distance in the interval $(0, x^*)$. Ultimately, however, T_f is approached and m_B drives $q(x)$ to zero. Our approximation assumes that the rate of increase of k_G is matched by the rate of decrease of m_B at least out to some distance $x_1 \gg \lambda/MC_p$, i.e., $q(x)$ is assumed constant from the surface to x_1 . Equation (6) can then be written

$$\begin{aligned} \phi_G &\doteq q(0) \int_0^{x_1} e^{-\frac{MC_p}{\lambda} x} dx + \int_{x_1}^{\infty} e^{-\frac{MC_p}{\lambda} x} q(x) dx \\ &\doteq \frac{\lambda q(0)}{MC_p} - e^{-\frac{MC_p}{\lambda} x_1} \left[\frac{\lambda q(0)}{MC_p} - \int_0^{\infty} e^{-\frac{MC_p}{\lambda} y} q(x_1+y) dy \right] \quad (45) \end{aligned}$$

where $y = x - x_1$. Since we have assumed that $x_1 \gg \lambda/MC_p$, the second term in Eqn. (45) will be small due to the exponential and can be neglected (assuming also that $q(x)$ does not increase too rapidly for $x > x_1$). Eqn. (45) then

becomes

$$\phi_G \doteq \frac{\lambda q(o)}{MC_p} \quad (46)$$

This formalism is the same as that used in the steady-state component of the KTSS non-steady combustion theory.¹⁶ However, in that theory the equivalent of Eqn. (46) was not used to calculate *a priori* the steady-state burning behavior. Instead, the pressure dependence of the term $\lambda q(o)/C_p$ was deduced semi-empirically by imposition of an assumed burning rate law of the form $M=ap^n$.

Equation (46) also bears a formal resemblance to a simple burning rate theory developed by Kubota, et al.¹⁷ as a baseline in their study of double base catalysis. In that work, however, $q(x)$ was assumed constant throughout the flame zone. The constant value was then evaluated, not at the interface, but at the flame temperature and density. In order to avoid the result that $q(T_f) = 0$, because the reactant mass fraction is zero at the flame temperature, the mass fraction appears to have been arbitrarily reset to its initial value. The net result is a model which is identical to the low heat-feedback limit of the (zero diffusion) CTRR formulation (see Section IVA1).

Evaluating Eqn. (11) at $x = +\infty$ and substituting the result into Eqn. (46) gives ϕ_G as an explicit function of T_s , M , and m_B^{+0} . This enables a Level I solution to be found by simultaneously solving Eqns. (21), (23) and either Eqn. (19) or (24), depending on the desired surface decomposition mechanism, for the three unknowns T_s , M , and m_B^{+0} . Thus, the net effect of the QCHR approximation is to replace a difficult non-linear differential equation problem with a relatively simple algebraic one.

A Level II formulation (see Section IIF) of the QCHR approximation can be shown to give

$$\phi_G = \frac{\lambda Q_G (\bar{W} P m_B^{-0}) A_G e^{-E_G/RT_s}}{MC_p R T_s^2} \quad (\text{Level II}) \quad (47)$$

Unlike the CTRR and DFHR models the criterion for validity of the QCHR assumption is not clearly expressible in terms of limiting values of the input parameters. Rather, the specification is placed on the behavior of an integrated quantity, $q(x)$, which to some degree involves all of the input parameters. Since the kinetics parameters pertinent to burning propellants

¹⁶H. Krier, J.S. Tien, W.A. Sirignano and M. Summerfield, "Nonsteady Burning Phenomena of Solid Propellants: Theory and Experiments," AIAA Journal, Vol. 6, p. 278 (1968).

¹⁷N. Kubota, T.J. Ohlemiller, L.H. Caveny and M. Summerfield, "The Mechanism of Super-Rate Burning of Catalyzed Double Base Propellants," AMS Report No. 1087, Princeton University, March 1973.

are not reliably known, this method of specification may not represent a disadvantage. In fact, observations of the burning process inevitably sense integrated quantities, so that it may be easier to judge the appropriateness of the QCHR approximation than those which specify a limiting value of E_G . This approach is illustrated in the next section.

D. Review of Experimental Evidence for Gas Phase

The most detailed experimental investigations of the thermal wave structure in solid propellant combustion have been measurements of temperature profiles obtained by imbedding small thermocouples in propellant samples. Interpretation of these measurements is beset by problems such as thermal inertia, thermal conduction through the junction leads, and determining when the thermocouple emerges from the solid. Because of the steep temperature gradients actually measured, these problems, which are still not fully resolved, can present serious obstacles to extracting accurate temperature profiles from the raw data. Nonetheless, these measurements can provide valuable qualitative and some quantitative insight as to the nature of the solid propellant burning process. They have, for example, revealed the existence of distinct plateaus in the spatial temperature profile in the gas phase for single and double base propellants.^{17,18,19,20} The generally accepted picture (for these propellants) has emerged of two exothermic kinetic stages — one immediately adjacent to the surface (fizz zone) and one associated with the visible flame. These two zones are separated by a "dark" zone characterized by temperature plateau where presumably the flame zone reactants are created in thermoneutral reactions.

Evidence as to whether or not the visible flame reactions affect the burning rate is mixed. One test is to look for a kink in the $\log r$ vs. $\log P$ curves through the pressure range where the visible flame first appears. Crawford, et al.²¹ and Heath and Hirst²² both made particular note of the

¹⁸R. Klein, M. Mentster, G. Von Elbe and B. Lewis, "Determination of the Thermal Structure of a Combustion Wave by Fine Thermocouples," *J. Phys. & Colloid Chem.*, Vol. 54, p. 877 (1950).

¹⁹C.A. Heller and A.S. Gordon, "Structure of the Gas Phase Combustion Region of a Solid Double Base Propellant," *J. Phys. Chem.*, Vol. 2, p. 773 (1955).

²⁰A.A. Zenin, "Structure of Temperature Distribution in Steady-State Burning of a Ballistite Powder," *Fizika Goreniya i Vzryva*, Vol. 2, p. 67 (1966).

²¹B.L. Crawford, Jr., C. Huggett and J.J. McBrady, "The Mechanism of the Burning of Double-Base Propellants," *J. Phys. Colloid Chem.*, Vol. 54, p. 854 (1950).

²²G.A. Heath and R. Hirst, "Some Characteristics of the High Pressure Combustion of Double-Base Propellant," *Eighth International Symposium on Combustion*, The Combustion Institute, p. 711 (1962).

absence of such a kink. Suh and Clary²³, on the other hand, found a prominent slope change at the onset of the visible flame. All of the measurements were made with double-base propellants but compositions varied.

While the energy release in the flame zone is substantial²¹, we shall assume that it contributes negligibly to ϕ_G . Further we assume that the fizz zone reaction or reactions can be adequately represented by our single gas phase reaction $B \rightarrow C$. Thus T_f is to be taken as the dark zone temperature and not the final propellant flame temperature.

Klein, et al.,¹⁸ first used the temperature profiles generated by imbedded thermocouples to estimate the heat release function $q(x)$ from the energy conservation equation (Eqn.(4)). His results for nitrocellulose strands at 28 atm pressure are given in Fig. 2 which shows the inferred fizz zone energy release. We have taken the thermocouple data of Kubota, et al.,¹⁷ for a laboratory double-base propellant PNC/TMETN (particulate nitrocellulose and trimethylolethane trinitrate) which has similar burn rate characteristics as NC/NG (nitrocellulose and nitroglycerin) and constructed the function $q(x)$ in the manner of Klein, et al.¹⁸ This function is computed at 1.2 atm and 21 atm and shown in Figs. 3 and 4, respectively.

Since the QCHR approximation is couched in terms of $q(x)$, the "empirical" $q(x)$ functions can be used to test the model directly. The CTRR and DFHR Models have also been described in terms of $q(x)$ for this same purpose.

Using Eqns. (5), (28), and (32) or (34) one can see that $q(x)$ in the CTRR Model is a monotonic decreasing function of x . This behavior is not well approximated in Figures 2-4. The rising nature of $q(x)$ results from a reaction rate which is increasing (due to temperature rise) at a faster rate than the reactant is being consumed.

The self-consistency of the DFHR Model can be partially tested by integrating the $q(x)$ functions over x to obtain an estimate of $Q_G^{Mn\bar{B}^0}$ (Eqn. (37)), then using the position of the $q(x)$ peak as x^* . A "model" value for ϕ_G can then be computed from Eqn. (39). This can be compared with the "empirical" value of ϕ_G obtained by performing the integration in Eqn. (6). The results of such a calculation are shown in Table 1. (The error associated with these integrations is on the order of 10% as judged by the self-consistency between the measured temperature gradient at the surface times λ and the integration over $q(x)$). Although the $q(x)$ curves in Figures 2-4 are not characterized by a small peak-width-to-standoff-distance ratio, the "model" and "empirical" values agree quite well. Not probed by this test, however, is the accuracy with which the actual flame standoff distance would be predicted by the idealized value as given by the Williams model¹⁵, for instance.

The constant q assumption of the QCHR model also appears to be at odds with the figures; however, the value of the model as an approximation depends on the extent to which $q(x)$ changes over the distance scale λ/MC_p . The QCHR model value of ϕ_G is obtained from Figures 2-4 using Eqn. (46). As shown in

²³N.P. Suh and D.L. Clary, "Steady-State Burning of Double-Base Propellants at Low Pressures," AIAA Journal, Vol. 8, p. 825 (1970).

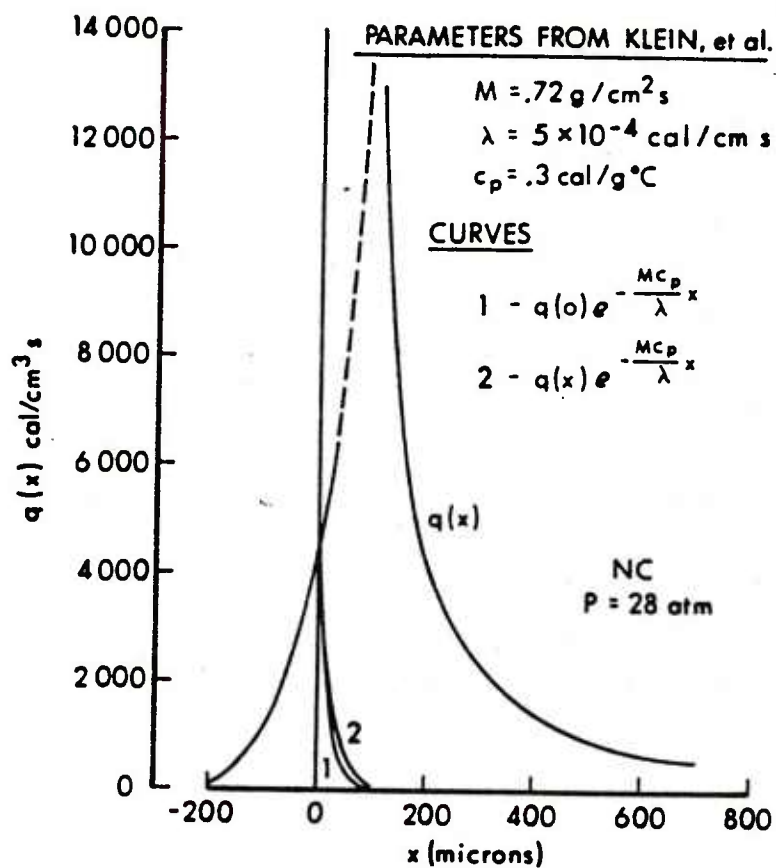


Figure 2. Empirical gas-phase heat release function calculated by Klein, et al.,¹⁸ for NC at 28 atm.

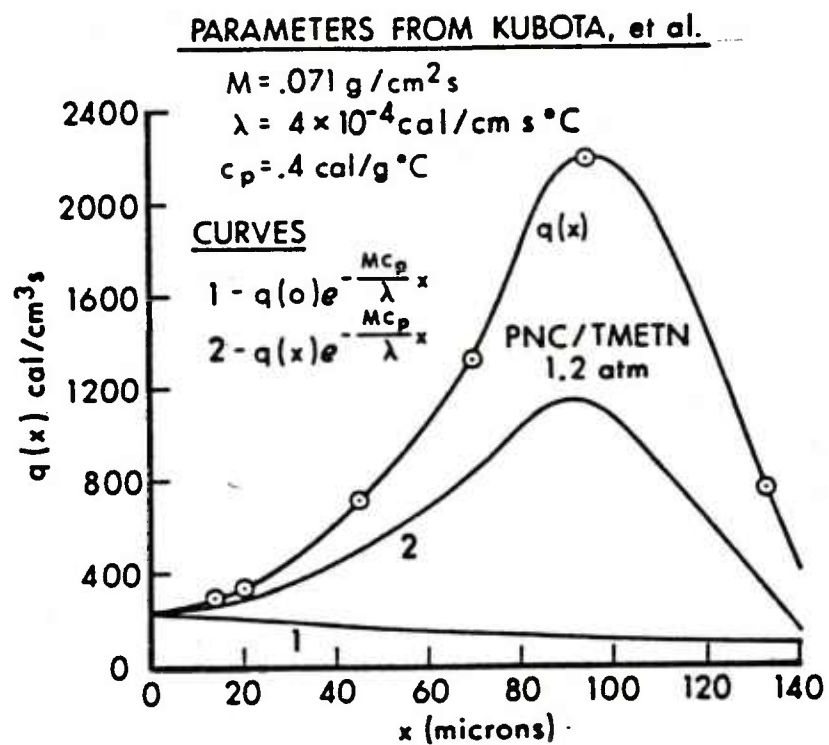


Figure 3. Empirical gas-phase heat release function based on data of Kubota, et al.,¹⁷ for PNC/TMETN at 1.2 atm.

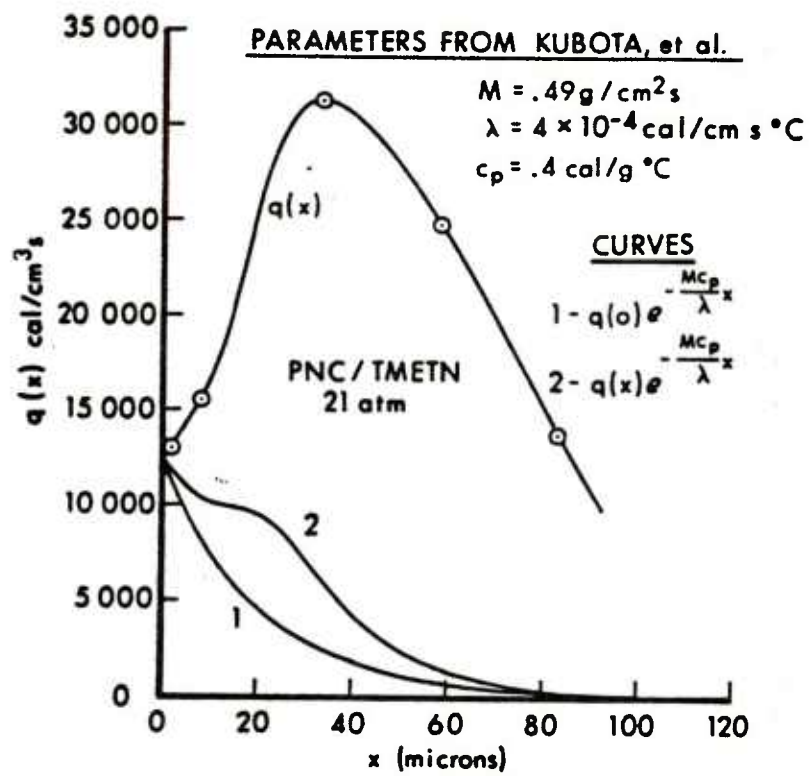


Figure 4. Empirical gas-phase heat release function based on data of Kubota, et al.,¹⁷ for PNC/TMETN at 21 atm.

TABLE 1. COMPARISON OF HEAT RELEASE MODELS
USING EMPIRICAL HEAT RELEASE FUNCTIONS

Propellant, Pressure	HEAT FEEDBACK VALUES ϕ_G (cal/cm ² sec)		
	Empirical	Delta Function (% Error)	QCHR (% Error)
NC ¹⁸ , 28 atm (Fig. 2)	12	3.2 (73%)	9.6 (20%)
PNC/TMETN ¹⁷ , 1.2 atm (Fig. 3)	8.7	7.9 (9%)	3.4 (60%)
PNC/TMETN ¹⁷ , 21 atm (Fig. 4)	43	43 (0%)	26 (40%)

Table 1, the QCHR values of ϕ_G seriously underestimate the empirical value in the low pressure case (Figure 3) but are quite credible at the higher pressures. The Kubota, et al.¹⁷ data did not extend to higher pressures but, taken together, Figures 3 and 4 might well represent a trend that the QCHR approximation improves with pressure. Since the basis of the approximation is that $q(x)$ remains relatively constant for a distance away from the surface on the order of λ/MC_p , it is equivalent to there being little curvature in the temperature profile out to this distance. Thus, if the temperature rises linearly away from the surface for a distance on the order of λ/MC_p , the QCHR model should give a reasonable approximation to ϕ_G . The thermocouple data of Zenin²⁰ for a NC/NG propellant (ballistite) give similar results as that of Kubota, et al.,¹⁷ at 20 atm pressure. Zenin²⁰ also obtained data at pressures up to 150 atm. At 50 atm the temperature rise appears to be quite linear to a distance well beyond λ/MC_p , tending to support the prospect of QCHR improving with pressure. At higher pressures the resolution is too coarse to judge the linearity of T.

In summary, the available thermocouple data gives little encouragement to the CTRR approximation since the shape of $q(x)$ over the region of influence is incorrectly predicted. The delta function formulation appears to be a reasonable idealization of $q(x)$, but we were unable to test the adequacy of the idealized flame standoff distance. The QCHR approximation appears to be reasonably consistent with the thermocouple data above ~ 20 atm for nitrate ester propellants. We caution, however, that comparisons with this data are made in part to demonstrate what we feel to be a promising analysis procedure. We have made no attempt to assess the reliability of the embedded thermocouple method for this purpose.

IV. ANALYTIC BURNING RATE EXPRESSIONS

In this section we shall mate the various approximations for ϕ_G with ϕ_S for different surface decomposition models in order to derive expressions for the burning rate. We are interested foremost in trying to determine the theoretical basis of the ubiquitous empirical burning rate laws which have been variously determined^{1,21} as

$$r = a + bP \quad (48)$$

$$r = bP^n \quad (49)$$

$$r = a + bP^n \quad (50)$$

where a , b , and n are constants determined from fits of these functional forms to the burning rate. In addition we shall be interested in the temperature

sensitivity of the burning rate at constant pressure which is defined by

$$\sigma_p = \frac{1}{r} \left(\frac{dr}{dT_o} \right)_p \quad (51)$$

where the subscript p denotes that the derivative is taken while holding the pressure constant. The most common empirical representation of σ_p is^{1,24}

$$\sigma_p = \frac{c}{d - T_o} \quad (52)$$

where the constants c and d are fitting parameters. In order to maintain a maximum of analytic flexibility, we shall confine ourselves to estimates based on Level II approximations in every case.

A. Pyrolysis Decomposition Mechanism

As discussed in Section IIE one may obtain a value for the burning rate at some (T_o, P) by equating ϕ_S (Eqn. 18) to the model of ϕ_G of interest (Eqns. 33, 35, 44, or 47). Using the pyrolysis law (Eqn. 19) to eliminate M as an independent variable, ϕ_S can be expressed as a function of T_s and T_o only. Any of the models for ϕ_G can be expressed as a function of T_s and P only. For the CTRR and DFHR models in which ϕ_G depends explicitly on T_f , T_f may be found as a function of T_s by solving the equation

$$T_f = T_s + (Q_{GB}^{m-o} - \phi_G(T_s, T_f)/M)/\bar{C}_p$$

which equates the heat retained in the gas to the difference between the total gas-phase heat release and the heat lost from the gas to the surface by conduction. One then must find that value of T_s for which $\phi_S(T_s, T_o) = \phi_G(T_s, P)$ and use the pyrolysis law to obtain the burning rate.

It is informative to illustrate this matching process graphically by plotting both ϕ_S and ϕ_G as a function of T_s . This is done in a schematic fashion in Figure 5, where the intersection of the ϕ_S and ϕ_G curves occurs at the surface temperature pertinent to either (T_o, P_1) or (T_o, P_2) . Note that this construct effects a separation of the influences of pressure and initial temperature on the problem since ϕ_G does not depend on T_o and ϕ_S does not depend on P . For values of T_s not close to T'_s (where $T'_s \equiv T_o + Q_s/\bar{C}_p$ is the surface temperature for which no gas-phase heat feedback is required), ϕ_S is dominated by the exponential character of M (by Eqn. (19)); but for $T_s \sim T'_s$

²⁴K.K. Andreyev and A.F. Belyayev, Theory of Explosive Substances, Moscow (1960), DDC #AD 6435971.

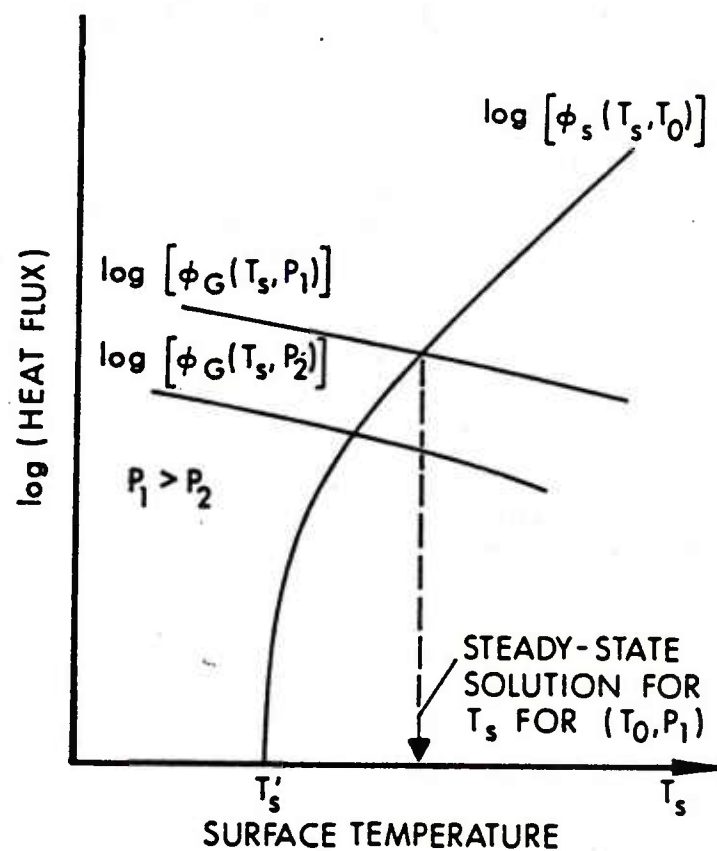


Figure 5. Illustration of matching condensed and gaseous phase heat fluxes in order to obtain surface temperature for a given (T_0, P) in the case of a pyrolysis mechanism.

the $(T_s - T_s')$ term dominates, driving ϕ_s to zero as $T_s \rightarrow T_s'$. The dependence of ϕ_G on P is less complicated in that varying P serves only to translate the $\phi_G(T_s)$ curve vertically with respect to $\phi_s(T_s)$. To illustrate this, two ϕ_G curves are drawn in Figure 5 for the different pressures P_1 and P_2 (where $P_1 > P_2$). In the limit of sufficiently low pressures, the intersection of ϕ_G and ϕ_s occurs at an essentially constant value of $T_s \doteq T_s'$. Thus in the low pressure limit $M \rightarrow$ constant, that constant depending only upon M_0 and T_s' and not on the gas-phase parameters. In this limit, it is fair to say that the solid reaction is rate limiting. However, at high pressures (where M dominates ϕ_s) neither the gas nor the solid phase reaction alone can be said to be rate limiting, i.e., M will depend on changes in either the solid or gas-phase reaction rates (or heats).

1. CTRR Approximation to ϕ_G

In order to discuss the burning rate derived from the CTRR approximation to ϕ_G , we first show that Eqns. (33) and (35) can be placed in a similar form. We introduce the following analytic approximation for the exponential integral

$$E_2(z) \doteq \frac{e^{-z}}{1+z}.$$

This approximation gives the correct limiting values for E_2 at $z=0$ and $z \rightarrow \infty$ and overestimates E_2 by a maximum of 25% at $x=0.5$. Using this expression to reduce Eqn. (35), one can show that for $v=1$ or 2 ,

$$\phi_G \doteq \frac{Q_G m_B^{-o}}{\left[1 + \frac{M^2 \bar{C}_p}{\lambda R_o (m_B^{-o})^{v-1}} \right]} \quad (53)$$

where R_o is defined in Eqn. (29). Equating this ϕ_G to ϕ_s from Eqn. (18), solving for M produces the expression

$$M = \left\{ \frac{\lambda \bar{W}^v A_G (m_B^{-o})^{v-1} e^{-E_G/RT_f}}{\bar{C}_p R^v T_f^v} \left[\frac{Q_G m_B^{-o}}{\bar{C}_p (T_s - T_o - Q_s/\bar{C}_p)} - 1 \right] P^v \right\}^{\frac{1}{2}} \quad (54)$$

For most propellants it can be argued that $E_s/RT_s \gg 1$, in which case the variation of $\exp(-E_s/RT_s)$ with T_s is enormous compared with that of $(T_s - T_s')$ in the high pressure limit where $T_s \neq T_s'$. The pressure dependence of the burn rate M is therefore seen to be approximately $M \propto p^{v/2}$, a dependence often

associated with simple propellant combustion models.^{8,13,17,25,26} This $p^{v/2}$ dependence is a fairly rigorous result²⁷ for a premixed laminar flame with a reaction of order v , though the boundary conditions in that case are different than for a solid propellant. Combining the low and high pressure limiting behaviors, M as calculated in the CTRR approximation for a pyrolytic mechanism has approximately the same overall pressure dependence as the form

$$M = a_1 + b_1 p^{v/2}$$

where

$$a_1 = M_o \exp \left[- \frac{E_s}{R(T_o + Q_s/\bar{C}_p)} \right]$$

and b_1 decreases slowly with increasing pressure.

The temperature sensitivity in the high pressure limit can be obtained as follows.

$$\sigma_p = \frac{1}{M} \frac{dM}{dT_s} \frac{dT_s}{dT_o}.$$

Eqn. (19) may be used to obtain the derivative of M with respect to T_s . Eliminating M between Eqns. (19) and (54) gives an expression containing the variables T_s , T_o , and T_f . T_f can be written as a function of T_o in Level I generality by solving the equation $h_A(T_o) = h_C(T_f)$. For the case of constant and equal specific heats, the result is

$$T_f = T_o + \frac{Q_T}{\bar{C}_p} \quad (55)$$

where $Q_T \equiv (Q_s + m_B^{-o} Q_G)$ is the total heat released in both the solid and gas phases (through the fizz zone, for example) per unit mass of propellant. Using this relation to eliminate T_f as well, one obtains an equation involving only T_s and T_o . Taking the natural logarithm of both sides of this equation

²⁵ Ya. B. Zeldovich, "On the Combustion Theory of Powder and of Explosives," *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki*, Vol. 12, p. 498 (1942).

²⁶ S.F. Boys and J. Corner, "The Structure of the Reaction Zone in a Flame," *Proc. Roy. Soc. (London)*, Vol. A197, p. 90 (1949).

²⁷ J.O. Hirshfelder, C.F. Curtiss and R.B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley & Sons, Inc., New York, p. 765 (1964).

then performing an implicit differentiation with respect to T_o yields

$$\frac{dT_s}{dT_o} = \frac{RT_s^2}{E_s} \left[\frac{\frac{\beta/2}{(T_s - T'_s)} + \frac{E_G}{2RT_f^2} - \frac{v}{2T_f}}{1 + \frac{RT_s^2}{2E_s(T_s - T'_s)}} \right]$$

where

$$\beta \equiv \frac{1}{1 - \frac{\bar{C}_p(T_s - T'_s)}{Q_{GmB}^{-o}}} = \frac{1}{1 - \frac{\phi_G}{Q_{GmB}^{-o}}}.$$

The parameter β is related to the fractional heat feedback from the gas phase, being large when this fraction is large and close to unity in the limit of low fractional heat feedback. Two limits can be identified. For high fractional heat feedback, i.e.,

$$\frac{\phi_G}{Q_{GmB}^{-o}} \sim 1,$$

$$\frac{\partial T_s}{\partial T_o} \sim 1$$

and σ_p in this limit can be shown to be

$$\sigma_p = \frac{E_s}{RT_s^2} \quad (56)$$

We do not expect this limit to be significant in a practical sense, however, since if $\phi_G = Q_G M_B^{-O}$, T_s would approach a constant (as can be seen by using Eqn. (18)) and M would therefore lose its pressure dependence. Experimentally, most homogeneous propellants show no sign of departing from $M \propto p^n$ at high pressure. For low to moderate fractional heat feedback, and $E_s/RT_s \gg 1$, the leading terms in σ_p become

$$\sigma_p \doteq \frac{\beta/2}{[(T_s - Q_s/\bar{C}_p) - T_o]} + \frac{E_G}{2R(T_o + Q_T/\bar{C}_p)^2} - \frac{\nu}{2(T_o + Q_T/\bar{C}_p)} \quad (57)$$

The first term on the right hand side of Eqn. (57) is similar to the empirical form of Eqn. (52). However, while the third term on the RHS of Eqn. (57) can likely be neglected compared with the second term, the second term cannot be expected to be negligible. For example, for a NC-based propellant, taking T_f to be $\sim 1500^\circ K$ ^{17,18,20} and E_G as ~ 15 kcal/mole (representative of NO_2 -aldehyde reactions^{28,33}), $E_G/2RT_f^2 = .0017$, which is of the same magnitude as σ_p .²⁹ Note also that the second term decreases with increasing T_o contrary to the empirical behavior in Eqn. (52).

2. DFHR Approximation to ϕ_G

Equating Eqns. (18) and (44) and solving for M produces the following result applicable to the high pressure limit (i.e., where $T_s \neq T_s'$). The term in brackets can be expected to decrease slowly with pressure.

$$M = \left\{ \frac{\lambda A_G e^{-E_G/RT_f}}{\bar{C}_p} \ln \left[\frac{Q_G m_B^{-O}}{\bar{C}_p (T_s - T_s')} \right] \right\}^{\frac{1}{2}} \left(\frac{\bar{W}P}{RT_f} \right)^{\nu/2} \quad (58)$$

Again at low pressures M approaches the same constant (a_1) as was found in Section IVA1.

For the δ -function case one finds that

²⁸F.H. Pollard and R.M.H. Wyatt, "Reactions between Formaldehyde and Nitrogen Dioxide," *Trans. Faraday Soc.*, Vol. 45, p. 760 (1949).

²⁹L. Shulman, J. Harris, C. Lenchitz, "Burning Characteristics of Standard Gun Propellants at Low Temperature ($21^\circ C$ to $-52^\circ C$)," *Tech. Report FRL-TR-41, Picatinny Arsenal, Dover, NJ* (1961).

$$\frac{dT_s}{dT_o} = \frac{RT_s^2}{E_s} \left\{ \frac{\frac{\xi/2}{(T_s - T_s')} + \frac{E_G}{2RT_f^2} - \frac{\nu}{2T_f}}{1 + \frac{RT_f^2 \xi}{2E_s(T_s - T_s')}} \right\}$$

where

$$\xi \equiv \left\{ \ln \left[\frac{Q_{GMB}^{-o}}{\bar{C}_p (T_s - T_s')} \right] \right\}^{-1}.$$

Like β of the preceding section, ξ is related to the fractional heat feedback from the gas phase and is of order unity as long as ϕ_G is not very near Q_{GMB}^{-o} . We previously argued that this circumstance is unlikely to be encountered over the conditions of practical interest. Therefore in the high pressure limit and for $E_s/RT_s \gg 1$, the leading terms in the temperature sensitivity are

$$\sigma_p \doteq \frac{\xi/2}{[(T_s - Q_s/\bar{C}_p) - T_o]} + \frac{E_G}{2R(T_o + Q_T/\bar{C}_p)^2} - \frac{\nu}{2(T_o + Q_T/\bar{C}_p)}. \quad (59)$$

The temperature sensitivity for the BDP monopropellant model has been previously derived.^{13,30} Although it has not been expressed in the same form as Eqn. (59) above, the two expressions can be shown to be equivalent except that the third term on the RHS of Eqn. (61) is absent in the BDP formulation because of a slight difference in definition of x^* between Ref. 11 and Refs. 12, 13 and 30. Coates³¹ has obtained an expression of σ_p based on a laminar-flame-theory model. Its dominant term is equivalent to the second term on the RHS of Eqn. (59). In laminar-flame-theory models^{3,15,26,31} the burning rate is determined entirely from the conditions prevailing in the thin reactive-diffusive zone at x^* . There being no explicit dependence of M on T_o or T_s , only the implicit dependence of T_f on T_o remains to govern the temperature sensitivity. This is the same source of the last two terms in Eqn. (59). As previously noted

³⁰M.W. Beckstead and K.P. McCarty, "Calculated Combustion Characteristics of Nitramine Monopropellants," 13th JANNAF Combustion Proceedings, CPIA Publication No. 281, Vol. I, pp. 57-58 (1976).

³¹R.L. Coates, "An Analysis of a Simplified Laminar Flame Theory for Solid Propellant Combustion," Combustion Science and Technology, Vol. 4, p. 1, (1971).

the dependence of these terms on T_0 is qualitatively different than that of the empirical Eqn. (52).

3. QCHR Approximation to ϕ_G

Requiring Eqns. (18) and (47) to be equal and utilizing Eqn. (19) leads to

$$M = M_0 \left[\frac{\lambda Q_G A_G}{M_0^2 \bar{C}_p^2 (T_s - T_0 - Q_s / \bar{C}_p)} \left(\frac{\bar{W} P m_B^{-o}}{RT_s} \right)^v \right]^{\frac{E_s}{2E_s - E_G}} \quad (60)$$

in the high pressure limit and the constant value a_1 (Section IVA1) for sufficiently low pressures. The pressure exponent indicated in Eqn. (60) is

$$n = \frac{v E_s}{2E_s - E_G} \quad (61)$$

for high pressures. It is of considerable interest that this pressure index should be explicitly coupled with the solid and gas phase activation energies as well as the reaction order. An expression such as Eqn. (61) has potential value to performance-tailoring efforts. It also exemplifies the value of an analytically tractable idealization in making a connection between practical burning rate behavior and more fundamental processes which might be characterized independently of burning rate.

The variation of T_s with T_0 can be shown to be

$$\frac{dT_s}{dT_0} = \frac{RT_s^2}{E_s} \left[\frac{\left(\frac{\xi E_s}{2E_s - E_G} \right)}{T_s - T_s'} \right]$$

where

$$\zeta \equiv \left[1 + \frac{v RT_s}{(2E_s - E_G)} + \frac{RT_s^2}{(2E_s - E_G)(T_s - T_s')} \right]^{-1}$$

Since $(2E_s - E_G)$ is of order E_s , in the high pressure limit and for $\frac{E_s}{RT_s} \gg 1$,

ζ is close to unity. Therefore the leading term in σ_p is

$$\sigma_p \doteq \frac{\left(\frac{E_s}{2E_s - E_G} \right)}{[(T_s - Q_s/\bar{C}_p) - T_o]} \quad (62)$$

Thus the temperature sensitivity is also seen to depend explicitly on the solid and gas phase activation energies and in the same mutual relationship as for the pressure exponent. Since T_s depends strongly on E_s (which can be seen by equating Eqns. (19) and (60) and solving for T_s), the QCHR model suggests that one might be able to lower both the temperature sensitivity and the pressure exponent of a propellant by increasing its E_s (providing of course that the gas phase reactions retain similar activation energies and the surface heat release does not change much).

B. Evaporation Decomposition Mechanism

In adapting the evaporation law (Eqn. 20) to a Level II treatment (i.e., no diffusion) we assume that $m_B^{-o} = 1$ so that $P_B = P$. Thus T_s is a function of P alone. Also Q_s must be reinterpreted as the heat of transformation (Q_v) and will have the opposite sign as T_o , as for example in the redefinitions

$$T_s' \equiv T_o - Q_v/\bar{C}_p \quad \text{and} \quad Q_T \equiv Q_G - Q_v.$$

Since ϕ_S now depends on P (through T_s) as well as T_o , it is no longer possible to effect a separation of the influences of T_o and P as was done in the pyrolysis case. Furthermore, making the reasonable assumption that the surface temperature will never fall below T_o , it is evident that ϕ_S does not go to zero at low pressures (due to sign change on Q_v) so that the burning rate will not approach a constant at low pressures as was found for the pyrolysis mechanism. The burning rates and temperature sensitivities for the different ϕ_G models are obtained as follows.

1. CTRR Approximation to ϕ_G

The burning rate for the evaporation mechanism coupled with the CTRR ϕ_G is obtained by equating Eqns. (18) and (53) and solving for M . One obtains

$$M = \left\{ \frac{\lambda \bar{W}^v A_G (m_B^{-o})^{v-1} e^{-E_G/RT_f}}{\bar{C}_p R^v T_f^v} \left[\frac{Q_G m_B^{-o}}{\bar{C}_p (T_s - T_o + Q_v/\bar{C}_p)} - 1 \right] P^v \right\}^{1/2} \quad (63)$$

It can be expected that E_v/RT_s will normally be large so that the pressure

dependence of the bracketed quantity will be dominated by $P^{v/2}$ over the entire pressure range.

Since T_s does not depend on T_o , σ_p may be found directly by applying Eqn. (51) to Eqn. (63). The result is

$$\sigma_p = \frac{\beta/2}{[(T_s + Q_v/\bar{C}_p) - T_o]} + \frac{E_G}{2R(T_o + Q_T/\bar{C}_p)^2} - \frac{v}{2(T_o + Q_T/\bar{C}_p)} \quad (64)$$

2. DFHR Approximation to ϕ_G

For an evaporation mechanism the expression for M is similar to Eqn. (58) except that T_s depends directly on P (through Eqn. 20), and Q_s is appropriately redefined. The temperature sensitivity is obtained directly from the revised Eqn. (58). The result is the same as Eqn. (59) with appropriate redefinitions of T_s , Q_s , and Q_T .

3. QCHR Approximation to ϕ_G

Again equating Eqns. (18) and (47) but this time using the evaporation law (Eqn. 20), the following burning rate is derived

$$M = \left[\frac{\lambda Q_G A_G}{\bar{C}_p^2 (T_s - T_o + Q_v/\bar{C}_p)} \left(\frac{\bar{W}P_o}{RT_s} \right)^v \right]^{\frac{1}{2}} \left(\frac{P}{P_o} \right)^{\frac{v}{2}} + \frac{E_G}{2E_v} \quad (65)$$

appropriate to all pressures. The temperature sensitivity for this case is

$$\sigma_p = \frac{\frac{1}{2}}{[(T_s + Q_v/\bar{C}_p) - T_o]} \quad (66)$$

C. Discussion

Several comments are in order concerning the formulas just derived. First of all, in discussing pressure dependences we have consistently taken terms of the order of T_s as slowly varying provided $E_s/RT_s \gg 1$. This was done in order to obtain the essence of the functionalities involved. In all of the high pressure expressions for M and σ_p , T_s appears in the denominator. Since by either the pyrolytic or evaporative mechanism T_s will increase with increasing pressure, M will tend to increase with P somewhat less rapidly than the dominant pressure exponent would suggest. Typically, calculations in which T_s is obtained by solving the transcendental equation $\phi_s = \phi_G$ for a

pyrolysis mechanism resulted in a pressure exponent about 10-20% lower than that given by Eqn. (65). However, the P^n dependence of M is preserved, i.e., n is constant to a very good approximation in the high pressure limit. Such an accuracy is well within the range of usefulness in view of the considerable uncertainties involving the kinetic activation energies and possibly the model idealization itself.

We should also remark on our neglect of radiative losses from the surface of the solid. This radiative loss term would be added to the RHS of Eqn. (18) and would alter the character of ϕ_S as $T_S \rightarrow T_S'$ at low pressures. At values of P sufficiently low that the radiative loss term dominates ϕ_S , an abrupt deflagration limit (below which no steady-state solution exists) may result as has been discussed by Johnson and Nachbar³² and Buckmaster, et al.³ Crawford, et al.,²¹ notes such a apparent limit at about 1 atm for a double-base propellant (offering no explanation for it). Above this pressure they report that the burning rate is well described by Eqn. (50) with a non-zero value of a . The low pressure trend toward a constant value of M is therefore observed but the limit itself is probably masked by the eventual dominance of the radiative losses. It is also possible that the apparent decrease of Q_S with decreasing pressure observed in thermocouple experiments^{17,33} at low pressure may be due to radiative losses and not a change in reaction mechanism.

Collecting the results of this section we find that all of the gas-phase models considered lead to a burn rate of the form $M=a+bP^n$ for a pyrolysis mechanism and $M=bP^n$ for an evaporation mechanism. It is at least possible, therefore, to account for the experimentally observed functional forms of $M(P)$ using only a single gas-phase reaction. However, derivation of these functional forms are only a necessary and not sufficient condition for verifying the idealization, as is readily apparent from the diversity of gas phase approximations leading to the same functions for $M(P)$. This circumstance is simply a formal articulation of the widely recognized fact that a more detailed experimental constraint than the burning rate pressure dependence is needed to provide an effective test of a proposed combustion model.

The temperature sensitivity functions proved more responsive to the gas phase approximation used. Only the QCHR approximation led to a form of σ_p identical with the empirical form. The other two approximations are close, however, differing only by two additional terms which depend inversely on T_f . These extra terms are in general probably not negligible and may represent a significant variation of the CTRR and DFHR expressions for $\sigma_p(T_0)$ from the empirically deduced Eqn. (52).

³²W.E. Johnson and W. Nachbar, "Deflagration Limits in the Steady Linear Burning of a Monopropellant with Application to Ammonium Perchlorate," Eighth International Symposium on Combustion, The Combustion Institute, p. 678 (1962).

³³G. Lengellé, J. Duterque, C. Verdier, Z. Bizot and J. Trubert, "Combustion Mechanisms of Double Base Solid Propellants," Seventeenth Symposium (International) on Combustion, The Combustion Institute, p. 1443 (1978).

V. SUMMARIZING REMARKS

The steady combustion of homogeneous solid propellant is likely to involve a myriad of complexities whose details depend intimately on the particular propellant being studied. In spite of this inherent complexity, most of these propellants burn with a rate whose pressure dependence can be well represented empirically by one or the other of these simple forms

$$r = a + bP^n$$

$$r = bP^n$$

Their temperature sensitivities are commonly described by the empirical form

$$\sigma_p = \frac{c}{d - T_o}.$$

We have shown that these same formulas are explicitly derivable by assuming that the burning process consists of a single condensed-phase process and a single gas phase reaction. If the condensed-phase process is assumed to be endothermic (such as a phase change), the idealization leads to the form $r=bP^n$. For an exothermic condensed-phase process (such as a pyrolysis reaction) the idealization leads to the more general form $r=a+bP^n$ (which includes the possibility that "a" may be negligibly small). These same results for $r(P)$ were obtained even when rather different approximations to the heat-transport problem in the gas-phase were used. However, only for the new gas-phase approximation (QCHR) developed in this study was a temperature sensitivity formula recovered which is identical to the most common empirical form.

It was shown that many of the existing gas-phase approximations could be categorized into one of three basic assumptions regarding the behavior of the heat release function. This enables one to test the relative suitability of these assumptions for a given propellant by comparison with empirical heat release profiles calculated from temperature profiles. Such an approach has the advantage that no *a priori* estimates of kinetics constants are needed. The comparison was made using published embedded thermocouple records for nitrate ester propellants. Both the delta function heat release (DFHR) approximation and the quasi-constant heat release (QCHR) approximation appeared to be roughly consistent with the heat feedback one would compute from the transformed temperature profiles.

With regard to the applicability of the basic idealization considered, we have shown only that it is capable of accounting for the observed shapes of $r(P)$ and $\sigma_p(T_o)$. The significance of this conclusion, we feel, is that it was reached largely without recourse to specific values of the reaction rates, such rates being a matter of considerable controversy at the present time. On the other hand, the derived expressions for burning rate and temperature sensitivity differ in detail among the various models. Without concrete values for all the parameters one cannot judge the extent of this disagreement. For this reason the first task of a continued effort should be

to determine the relative and absolute accuracy of these models, possibly by comparison with numerical calculations for a few plausible data sets. In addition, further attention might profitably be given to assessing and extending the reliability of the embedded thermocouple technique as well as exploring techniques for extracting further information regarding the kinetics of the fizz zone reactions from the temperature profiles.

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LIST OF SYMBOLS

- A - propellant molecule label
- A_G - gas-phase reaction frequency factor
- B - gas-phase reactant label
- C - gas-phase product label
- C_p^B, C_p^C, C_p^C - specific heats at constant pressure in gas-phase
- C_s - specific heat at constant pressure in solid
- \bar{C}_p - specific heat for solid and gas phases ($C_s = C_p$)
- D_B, D_C, D - diffusion coefficients
- E_G - activation energy for gas-phase reaction
- E_s - activation energy for solid-phase reaction
- E_v - heat of transformation of solid to gas
- h_A, h_B, h_C - specific enthalpies of subscripted species
- $h_A^\circ, h_B^\circ, h_C^\circ$ - specific enthalpies at the thermodynamic reference state
- k_G - gas-phase reaction rate coefficient
- M - mass regression rate (mass flux)
- M_O - constant in pyrolysis surface decomposition mechanism
- m_A, m_B, m_C - mass fraction of subscripted species
- m_B^{-O}, m_B^{+O} - mass fraction of B evaluated at negative and positive sides of the solid/gas interface, respectively.
- N_1 - number of moles of B produced per mole of A
- N_2 - number of moles of C produced per mole of B which reacts
- n_B, n_C - number of moles per unit volume of subscripted species
- n - pressure exponent of burning rate
- P - total pressure
- P_B - partial pressure of B at positive side of solid/gas interface
- P_O - constant in evaporation surface decomposition mechanism

LIST OF SYMBOLS (Cont'd)

- P_1, P_2 - two unspecified particular values of total pressure
- Q_s - heat of reaction per unit mass for solid reaction (positive for exothermic)
- Q_G - exothermic gas-phase reaction heat per unit mass of B
- Q_T - total exothermic reaction heat (solid + gas) per unit mass of A
- Q_v - latent heat of transformation for $A \rightarrow B$ phase change mechanism (positive for endothermic)
- $q(x)$ - gas-phase heat release per unit volume per unit time at x
- $q_s(x)$ - solid-phase heat release per unit volume per unit time at x
- q_0 - constant in Delta Function Heat Release model
- R - universal gas constant
- $R(x)$ - mass of B reacting per unit volume per unit time at x
- R_0 - constant mass reaction rate in Constant Temperature Reaction Rate model
- r - linear regression rate of propellant surface.
- $T, T(x)$ - temperature at x
- T_0, T_s, T_f - initial, surface, and flame temperatures, respectively
- $T_s' = T_0 + Q_s/C_s$.
- T_1 - value of constant temperature in CTRR model
- u - local mass flow velocity in gas phase
- U - average mass flow velocity in gas phase
- V_B, V_C - local velocities of B or C (mass flow + diffusive)
- W_B, W_C - molecular weights of B and C
- \bar{W} - average molecular weight of mixture in gas-phase
- x - spatial variable
- x^* - gas-phase flame standoff position in DFHR model
- x_1 - a point in the gas-phase satisfying $x_1 \gg \frac{\lambda}{MC_p}$
- α - exponential coefficient in CTRR model

LIST OF SYMBOLS (cont'd)

β - term in $\frac{\partial T_s}{\partial T_o}$ expression for CTRR model

$\delta(x)$ - Dirac delta function

ζ - term in $\frac{\partial T_s}{\partial T_o}$ expression for QCHR model

λ - heat conductivity in gas-phase

λ_s - heat conductivity in solid-phase

ν - gas-phase reaction order

ξ - term in $\frac{\partial T_s}{\partial T_o}$ expression for DFHR model

ρ - local mass density in gas-phase

ρ_s - mass density of solid

ρ_f - mass density at $T = T_f$

σ_p - temperature sensitivity at constant pressure

τ - average reaction delay time in DFHR model

ϕ_G - heat flux from gas phase to surface supplied by gas-phase heat release

ϕ_S - heat flux from gas phase required by solid to maintain steady-state regression.

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